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## OBTAINING COMPOSITES BASED ON PYROPHYLLITE FROM THE KUL'-YURT-TAU DEPOSIT AND PHOSPHATE BINDER

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Changes of the phase and chemical compositions as well as the course of strengthening on heating of mixtures of pyrophyllitic raw material from the Kul'-Yurt-Tau deposit and, for comparison, the Ovruchskoe deposit with a phosphate binder are studied. It is shown that these materials exhibit similar behavior. The optimal amount of binder to obtain a strong pressed intermediate product is determined. The composites must be heat-treated at temperatures 500 – 600°C in order to attain water resistance and the required strength.

**Key words:** composite, pyrophyllite, phosphate binder, construction, heating, strengthening.

Studies of the technological characteristics of pyrophyllite show that it can be used as a raw material for producing ceramics and refractories [1]. In this connection, the chemical and mineralogical compositions as well as the physical-technical indicators of pyrophyllitic rock from the Kul'-Yurt-Tau deposit (Bashkortostan) have been studied in [2]. It was shown that the characteristics of these rocks are close to those of the previously used raw material obtained from the Ovruchskoe deposit (Ukraine), where mining has been stopped. In the present work we describe the results of subsequent research on the changes of the composition and structure occurring on heating as well as the course of strengthening of compositions of pyrophyllitic rocks, obtained from the Kul'-Yurt-Tau deposit, with phosphate binder.

Our objective here is to present the results of a study of the physical-chemical processes occurring when pyrophyllite is heated, which determine the possibilities of using pyrophyllitic raw material in the production of composites based on it.

Two forms of the most accessible and readily available raw material are chosen on the basis of previously obtained data [2] as the experimental objects: quartz – pyrophyllitic schists (KPPTS) and quartz – pyrophyllite – diaspore rock (PPS). Ovruchskoe pyrophyllite, which has been studied

most at the technological level, was used for comparison. The mineralogical composition of the raw material is presented in Table 1 [2].

**Evolution of Structure.** Thermographic studies have shown that when PPS samples are heated two endothermal effects with minima at 540 and 718°C are observed on the DTA curve (Fig. 1): the first is due to the removal of water from the crystal lattice of diaspore, sericite and kaolinite (first effect) and the second to pyrophyllite. An exothermal effect peaking at 982°C arises as a result of the crystallization of mullite from kaolinite as well as the phase transition  $\gamma \rightarrow \alpha$  of aluminum oxide formed as a result of the decomposition of diaspore. Thermal effects with maxima at 1190 and 1350°C appear as a result of the crystallization of mullite (1180°C) and silica (1350°C) from the products of decomposition of pyrophyllite.

The DTA curves of pyrophyllite from the Ovruchskoe deposit (PP) and of quartz-pyrophyllitic schists (QPPS) from

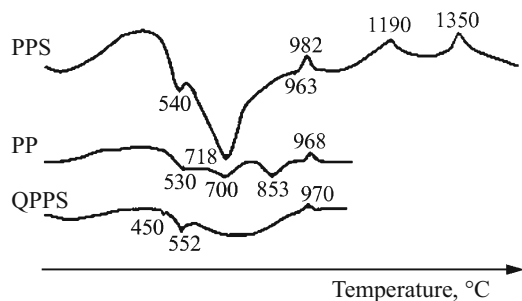
**TABLE 1.** Mineralogical Composition of Pyrophyllitic Raw Material [2]

Mineral	Mineral content, wt. %		
	PP	PPS	QPPS
Pyrophyllite	72 – 74	62 – 64	34 – 36
Kaolinite	3 – 4	10 – 12	2 – 3
Quartz	24 – 25	0.2 – 0.5	46 – 48
Diaspore	1 – 2	11 – 12	1 – 2
Sericite	3 – 4	2 – 3	3 – 4

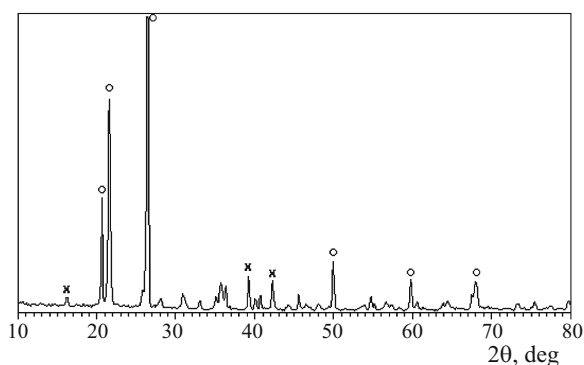
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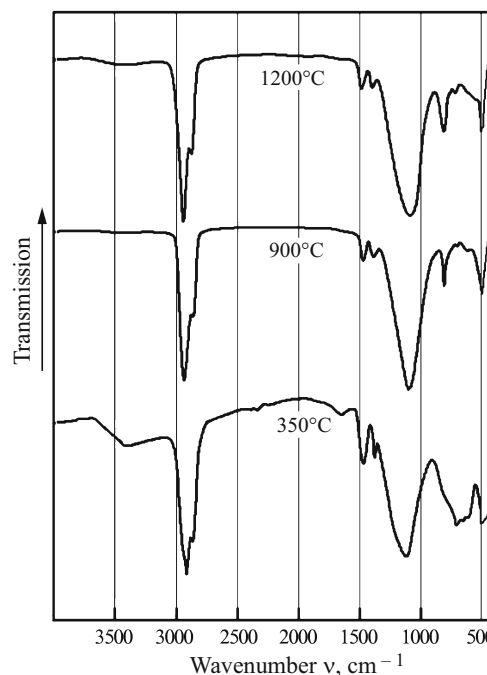
**Fig. 1.** DTA curves of PPS, PP and QPP samples. The rate of heating is 15 K/min.



**Fig. 2.** X-ray diffraction pattern of a QPPS sample after heat-treatment at 1350°C; (x) mullite; (o) cristobalite.

the Kul'-Yurt-Tau deposit exhibit endothermal effects at 450 and 552°C, which are due to phase transformation of quartz. This effect is reversible: when these samples are cooled an exothermal effect peaking at 546–548°C appears. The exothermal effect peaking at 970°C is weaker than on the DTA curve of pyrophyllite-diaspore rocks. This is explained by their comparatively lower content of kaolinite. The endothermal effect at 853°C in the DTA curve of pyrophyllite PP is stronger than on the QPPS and PPS curves; this is explained by the higher content of the pyrophyllitic phase in PP compared with samples of the pyrophyllitic raw material from the Kul'-Yurt-Tau deposit. Because of the lower content of pyrophyllite the endothermal effect on the region 500–900°C of the DTA curve of quartz-pyrophyllitic schists (QPPS) is weaker.

X-ray phase analysis of QPPS (Fig. 2) shows diaspore lines vanishing after 520°C and new lines attributable to different modifications of alumina appearing. The kaolinite and sericite lines vanish by 600°C, while the pyrophyllitic lines remain to 1050°C. All lines in the interval 1050–1150°C, except for those of alumina, vanish. Above 1200°C a glass phase (to 20–30%) manifests in the x-ray diffraction pattern and the lines appearing are due to the phases — mullite and silica in the form of cristobalite or tridimite. At 1325°C the tridimite lines vanish and the amount of the glass phase increases. At 1350°C the glass phase vanishes, while the



**Fig. 3.** IR transmission spectra of a QPPS sample after heat-treatment at 350, 900 and 1200°C.

mullite and cristobalite lines remain in the diffraction pattern. This is confirmed by the x-ray diffraction pattern which was obtained after heat-treatment of the sample at 1425°C and exhibits mullite and cristobalite lines (see Fig. 2).

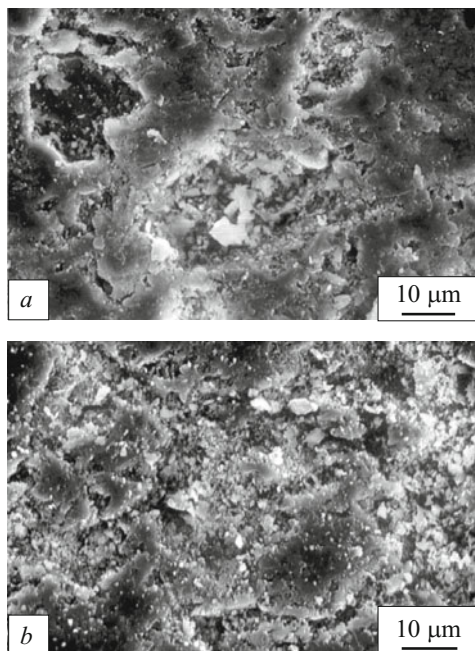
The IR spectra of minerals from the Kul'-Yurt-Tau deposit confirm the x-ray analysis of pyrophyllite (Fig. 3). According to the collection of absorption bands after the heat-treatment temperature 1200°C the spectrum obtained corresponds to the previously studied spectrum of PP [2].

The character of the change in the structure of the raw material during heat-treatment can be seen in Fig. 4 for the example of QPPS. Before heat-treatment (a) the structure is open, while after heating at 1200°C (b) densification as a result of sintering of aggregates of the initial raw material is evident.

The thermal analysis of pyrophyllite shows that mass loss starts at 200°C, reaching about 0.5% at 500°C. The total mass loss of the sample is about 8%. Since the water content in pure pyrophyllite is 5%, the remaining losses are most likely due to the decomposition of impurity minerals.

The weak endothermal effects observed at 940 and 1010°C are not directly related with water loss. The first one is due to the appearance of a liquid phase, engendered by the presence of alkali-metal oxide impurities. The liquid phase gradually evaporates on heating to 1050°C.

The IR spectra of pyrophyllite PP remain virtually unchanged on heating to 500°C. The IR spectra of the QPPS and PP samples obtained with temperature increasing to 900°C are similar. On subsequent heating single absorption bands due to peaks at 565 and 660 cm<sup>-1</sup> characteristic for



**Fig. 4.** Structure of quartz-pyrophyllitic raw material QPPS before (a) and after (b) heat-treatment at 1200°C.

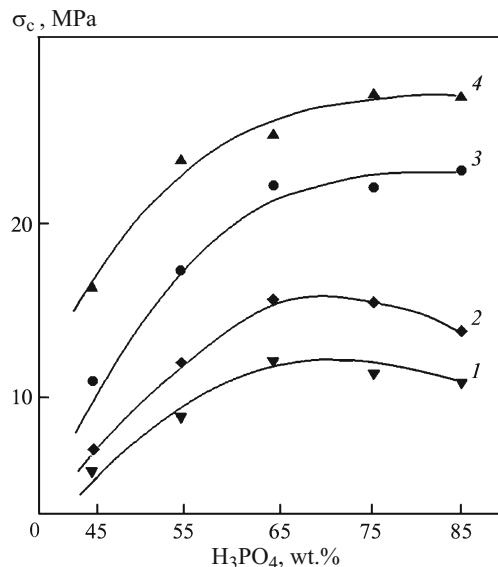
pyrosilicates appear in the spectra. The spectrum of samples heated at 1200°C contains wide unresolved absorption bands, which are typical for amorphous substances and undeveloped crystalline structures.

The studies show that thermal decomposition of pyrophyllitic raw material results in the formation of mullite and cristobalite, which determine the main properties of the material, including the small thermal expansion coefficient and high fire-resistance. The main phase, pyrophyllite, retains its crystalline structure to temperature 1050°C despite water loss at lower temperatures. The thermal behavior of QPPS and PPS is similar to that of Ovruchskoe pyrophyllite, which is used in refractories; therefore, they can be used for the same functional purposes. They can be used as a finely ground additive in heat-resistant materials. In addition, there is much promise in using pyrophyllitic raw material as a component (filler) in composite materials based on high-temperature inorganic binders, for example, phosphates.

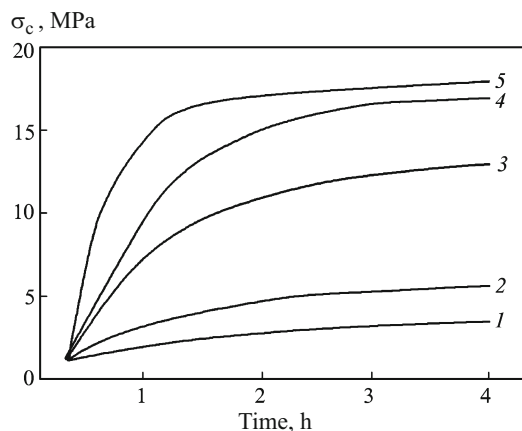
**Strengthening Behavior.** The structure-formation kinetics of the compositions was determined by measuring the compression strength of samples after isothermal soaking at different temperatures for 1 h depending on the amount of the phosphate binder. As the concentration of orthophosphoric acid (OPA) in the binding solution increases to 65 wt.% the strength of all compositions increases (Fig. 5).

A study of the strengthening kinetics of composites (Fig. 6) showed that the required strength of the samples is reached with heat-treatment above 300–400°C for 1–2 h.

It can be supposed on the basis of the data obtained that to fabricate compositions which are water-resistant under normal conditions they must be heat-treated for at least 1 h at



**Fig. 5.** Strength  $\sigma_c$  of QPPS-OPA composites versus the mass fraction of acid in the binding solution. The composites were processed at temperatures: 1) 500°C; 2) 800°C; 3) 1100°C; 4) 1200°C.



**Fig. 6.** Kinetics of the variation of the strength of QPPS-OPA compositions heat-treated at temperatures: 1) 100°C; 2) 200°C; 3) 400°C; 4) 500°C; 5) 600°C.

temperature above 400°C. Compositions with up to 25 wt.% acid exhibit the highest maximum technological strength.

The processes resulting in the formation of silicon phosphates as a result of the chemical interaction of acid with pyrophyllitic raw material lie at the heart of the strengthening of the experimental composites studied in this work; the rate and course of the chemical reactions depend on the heat-treatment regime. To check this, the compositions were heat-treated using different heating rates. The results show that the rate of heating during the initial period of heat-treatment strongly affects the strength of the samples. For each composition there exists an optimal rate of heating at which the maximum strength characteristics are obtained. Lowering the heating rate below the optimum does not appreciably af-

fect the strength of a composition. For example, for cylindrical samples with dimension  $d = 20 - 30$  mm and  $h = 30 - 40$  mm, obtained by semi-dry pressing, such a rate of heating to  $300^{\circ}\text{C}$  is about 1 K/min. To kiln samples with  $d = 40$  mm and  $h = 60$  mm it should be lowered to 0.2 – 0.8 K/min. At temperatures above  $300 - 500^{\circ}\text{C}$  the optimal rate of heating lies in the range 2 – 5 K/min for all samples.

In summary, the results obtained show that heating to  $500 - 600^{\circ}\text{C}$  produces a composite whose structure secures moisture resistance and technological strength. A further increase in strength is gained by increasing the temperature to  $900 - 1000^{\circ}\text{C}$ .

## SUMMARY

The present studies of the changes occurring in the phase and chemical compositions in the course of heating of pyrophyllites from the Kul'-Yurt-Tau deposit and for comparison the Ovruchskoe deposit showed that these materials behavior similarly. Therefore the first pyrophyllites are completely

adequate raw materials for the production of ceramics and refractories. The technological studies established the optimal amount of binder as well as the conditions for preliminary heat-treatment of the compositions. It was shown that pyrophyllite-containing materials, just as the other compositions based on phosphate binder, must be heat-treated at  $500 - 600^{\circ}\text{C}$  in order to water resistance and the required strength.

## REFERENCES

1. V. P. Perepelitsyn, Yu. E. Pivinskii, A. D. Burabov, et al., "Pyrophyllite from the Urals — a new refractory and ceramic raw materials in Russia," *Novye Ogneupory*, No. 9, 64 – 68 (2005).
2. V. S. Bakunov, A. R. Murzakova, R. U. Shayakhmetov, and L. V. Yakupova, "Pyrophyllitic raw material from the Kul'-Yurt-Tau deposit as a basis for ceramic composites," *Steklo Keram.*, No. 12, 23 – 27 (2011); V. S. Bakunov, A. R. Murzakova, R. U. Shayakhmetov, and L. V. Yakupova, "Pyrophyllitic raw materials from the Kul'-Yurt-Tau deposit as a base for ceramic composites," *Glass Ceram.*, **68**(11 – 12), 405 – 409 (2012).